

# Chapter 17 (AS-Level)

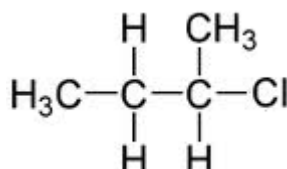
## Halogenoalkanes (Alkyl halides)

### General

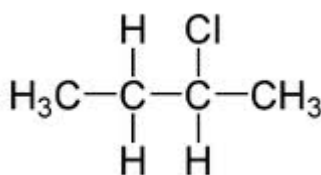
- They have a general formula of  $C_NH_{2N+1}X$ , where X is the halogen atom.
- They are known also as alkyl halides.
- They are hydrocarbons containing a halogen atom, joined to one or more carbon atoms in a chain.
- They are named by prefixing fluoro, Chloro, bromo and iodo to the name of the alkane, along with the number of the carbon atom it is attached to.

### Classification of halogenoalkanes

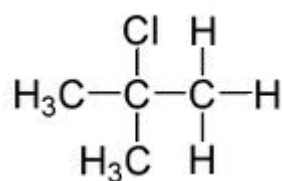
1. **Primary halogenoalkanes**, e.g. 1-chlorobutane, have a halogen atom covalently bonded to a carbon atom which has only one another carbon atom bonded to it.



2. **Secondary halogenoalkanes**, e.g. 2-chlorobutane, have a halogen atom covalently bonded to a carbon atom which has 2 other carbon atoms bonded to it.



3. **Tertiary halogenoalkanes**, e.g. 2-chloro-2-methylpropane, in which the halogen atom is covalently bonded to a carbon atom which has bonds with 3 other carbon atoms.



### Physical properties

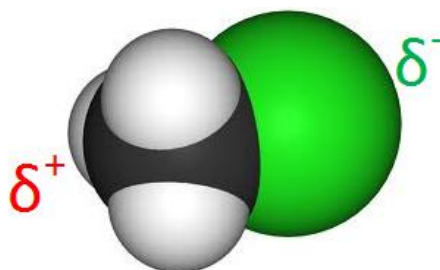
They are volatile liquids that don't mix with water.

### Nucleophilic substitution

All nucleophilic substitution reaction of alkyl halides involves the breaking of the bond between the carbon and the halogen atom.

### The polarity of the carbon-halogen bond

With the exception of iodine, all halogens are more electronegative than carbon. This means that the electron-pair in the C-X (X for halogen) bond will be dragged over to the halogen atom end, making a negative pole ( $\delta^-$ ) at the halogen and a positive pole at the carbon atom ( $\delta^+$ ).



### The strength of the C-X bond

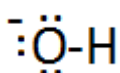
Some bond energies of different C-X bonds:

Bond	Bond energy (kJ/mol)	Bond	Bond energy (kJ/mol)
C-H	413	C-F	467
		C-Cl	346
		C-Br	296
		C-I	228

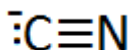
In all nucleophilic substitution reactions, the carbon-halogen bond must be broken. The harder it is to break, the slower the reaction. The bond energies decrease from Cl to I, so I is the most reactive.

### Nucleophilic substitution in primary alkyl halides ( $S_N2$ )

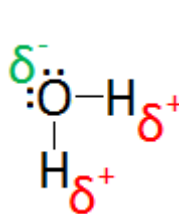
A nucleophile is a species that loves positive charges. They can be negative ions or have a strong  $\delta^-$  charge on their molecules. Examples include:



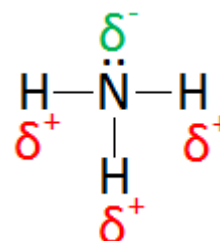
Hydroxide ion



Cyanide ion



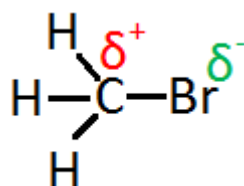
Water



Ammonia

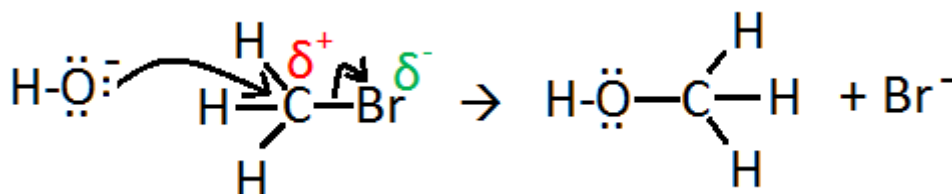
These contain at least one lone pair of electrons, or a very electronegative atom carrying the  $\delta^-$  charge.

With reaction with halogenoalkanes, for example, bromomethane, there is a polar bond between the Br and the C atoms:



If a nucleophilic ion approaches the molecule, for example,  $\text{OH}^-$  ion, it will be attracted to the carbon atom and repelled by the bromine atom.

It moves towards the carbon atom and begins to make a dative bond with it. The electrons in the C-Br bond start to be pushed towards the Br atom. This causes the Br atom to get expelled as a Br<sup>-</sup> ion.

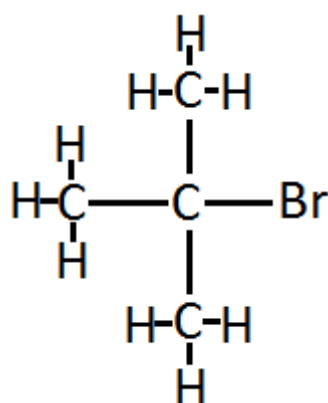


This is called SN2 reaction. The S for substitution, N for nucleophilic and 2 because the initial step of the reaction involved 2 species.

### Nucleophilic substitution in tertiary halogenoalkanes (S<sub>N</sub>1)

Why is a different mechanism necessary for tertiary alkyl halides?

When a nucleophile attacks a primary alkyl halide, it approaches the carbon atom from the side away from the halogen atom. With tertiary alkyl halides, this is impossible as the backside is cluttered with CH<sub>3</sub> groups.



Since any other approach is denied by the bromine atom, the reaction has to go by an alternative route or mechanism.

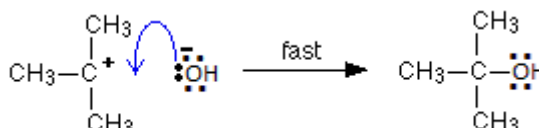
The reaction happens in two stages:

1. A small proportion of the alkyl halide ionizes into a carbocation and a halide ion (in this case it is Bromine ion).



This reaction is possible because the tertiary carbocations are more stable than secondary or primary alkyl halide carbocations. However, this reaction is slow.

2. However when the carbocation is formed, it would react immediately with the nucleophile as the nucleophile is attracted to it.



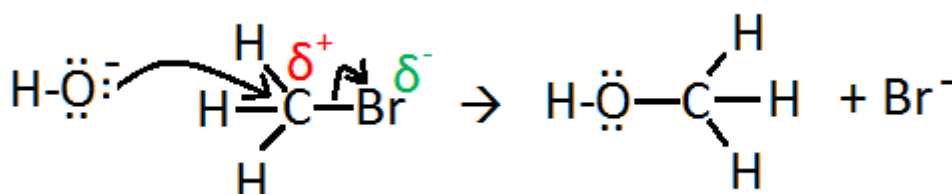
Because the reaction involves only one species, it is described as  $S_N1$  reaction.

### Hydrolysis

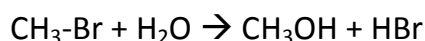
If an alkyl halide is heated under reflux with a solution of NaOH, the halogen atom is replaced by  $-OH$  and an alcohol is formed.

The solvent is usually a 50/50 mix of ethanol and water, as both hydrocarbons and other water-soluble substances are soluble in it.

The reaction is the same as before in nucleophilic substitution:

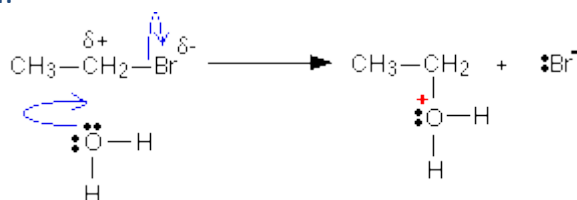


The same hydrolysis happens with water but it is slower:



The mechanism of the reaction with water:

#### 1. Nucleophilic substitution:

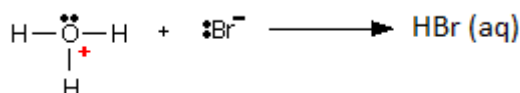


The reaction is slow as water isn't a good nucleophile as it does not carry a charge.

#### 2. Another water molecule removes one of the hydrogen atoms, to give an alcohol and an oxonium ion:



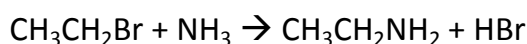
#### 3. The oxonium ion and the bromine ion from step 1 form hydrobromic acid (HBr):



The above is for primary alkyl halides. For tertiary alkyl halides, the reaction is the same as with normal  $S_N1$  reactions.

### Reaction with ammonia

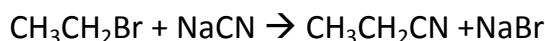
If alkyl halides are mixed with an excess of ethanolic ammonia and heated under pressure, amines are formed. For example, bromoethane will form ethylamine:



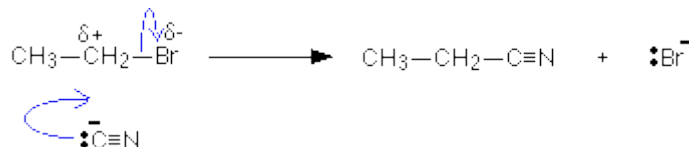
Ethylamine is a primary amine.

## Reaction with cyanide ions

When halogenoalkanes are heated under reflux with ethanolic sodium cyanide, nitriles are formed. For example:



This reaction contains one more carbon atom. The mechanism is:

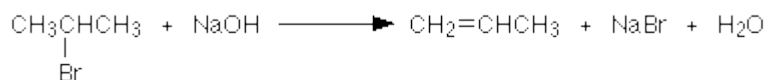


Because the mechanism involves collision between two species in the slow step (in this case, the only step) of the reaction, it is known as an  $\text{S}_{\text{N}}2$  reaction.



## Elimination reactions

2-bromopropane is heated under reflux with a concentrated solution of sodium or potassium hydroxide in ethanol. Heating under reflux involves heating with a condenser placed vertically in the flask to avoid loss of volatile liquids. Propene is formed and, because this is a gas, it passes through the condenser and can be collected.

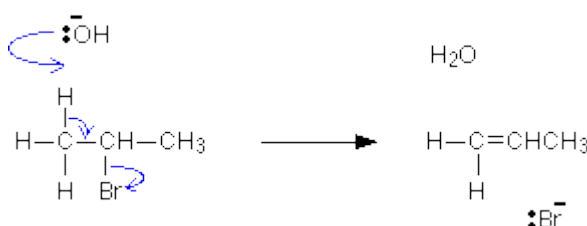


Everything else present (including anything formed in the alternative substitution reaction) will be trapped in the flask.

The mechanism is:

In elimination reactions, the hydroxide ion acts as a base - removing a hydrogen atom as a hydrogen ion from the carbon atom next door to the one holding the bromine.

The resulting re-arrangement of the electrons expels the bromine as a bromide ion and produces propene.



This is actually the elimination of hydrogen halide (in this case it is bromine) from the alkyl halide, leaving an alkane. The hydrogen halide reacts with the sodium ion present to form sodium bromide. This happens when a solution of pure alcohol with an alkali is used. This is because the rate of elimination is faster than the rate of nucleophilic substitution.

At lower temperatures, the substitution reaction proceeds at a faster rate.

### The uses of halogeno alkanes

CFCs are non-flammable and not very toxic. They therefore had a large number of uses.

They were used as refrigerants, propellants for aerosols, for generating foamed plastics like expanded polystyrene or polyurethane foam, and as solvents for dry cleaning and for general degreasing purposes.

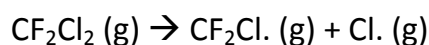
Unfortunately, CFCs are largely responsible for destroying the ozone layer. In the high atmosphere, the carbon-chlorine bonds break to give chlorine free radicals. It is these radicals which destroy ozone. CFCs are now being replaced by less environmentally harmful compounds.

Bromochlorodifluoromethane is used to stop extinguish fires. When combustible materials are ignited, free radicals are generated. These free radicals propagate many combustion reaction steps which produce even more free radicals.

The high temperatures break the compound down, producing bromine free radicals, which react with the free radicals produced from the combustion of the flammable material, extinguishing the fire.

### Problems with CFCs

CFCs are responsible for the depletion of the ozone layer. The high stability of the CFCs is one of the causes of the depletion of the ozone layer, which had enabled them to stay in the stratosphere a long time and build up there. When they reach the stratosphere they absorb ultraviolet light, which causes the photochemical dissociation of the carbon-chlorine compounds.



Very reactive chlorine free radicals are formed, which catalyse the decomposition of ozone into oxygen.

